

DIAMONDS IN THE CHEMICAL PRODUCTS OF DETONATION

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ABSTRACT

Diamonds have been found among the solid carbonaceous chemical products of high-explosive detonations. Explosives are fuel-oxidizer systems premixed on a molecular scale. This talk discusses some aspects of the chemical and hydrodynamic environment in which these diamonds form and some characteristics of the diamonds recovered. Diamonds have been recovered from detonations of composite explosives composed of trinitrotoluene (TNT) mixed with other powdered solid explosives, such as cyclo-trimethylenetrinitramine (RDX), triaminotrinitrobenzene (TATB), ammonium nitrate (AN), and nitroguanidine (NQ). The detonations were carried out in a 1.5-m³ tank, usually filled with 1 atm of Ar gas. Other explosive composites and one-component explosives have also been investigated. The diamonds have been characterized by transmission electron microscopy, x-ray diffraction, and various chemical means.

INTRODUCTION

Detailed knowledge of the chemical kinetics and equilibria of detonation has long been a desired, but elusive goal. One focus of this chemistry is the coagulation of carbonaceous solid (soot) from carbon initially present as the skeletal atoms of small organic molecules (typically consisting of 20 to 50 atoms). The "fuel" portion of the explosive molecule is the atoms of carbon and hydrogen, and the "oxidizer" is a number of nitro (-NO_2) groups. During detonation the fuel and oxidizer react to form water and oxides of carbon, the nitrogen forms N_2 , and the carbon left over forms the soot. At least that is what is visualized. Most of what is "known" of the chemistry of detonation is an intricately convoluted mixture of supposition, computer modeling, and calibration of the models against hydrodynamic measurements of detonating material.

A brief description of the detonation process is appropriate here. The literature affords a wealth of further detail (see, for example, Refs. 1-3). The hydrodynamic aspects of the detonation process are quite well known; that is, the density (d), pressure (P), and velocity (D) of the detonation wave for particular explosives are well established. Temperature and chemical composition are obtained as secondary information derived from a hypothetical equation of state of the detonation products calibrated against d-P-D data for a set of explosives. The equation of state must account for extreme nonideality (compressibility factors of 15-25) and must contain a mixing rule for the different molecular species in the products. Knowledge of the kinetics of the detonation process is almost entirely empirical.

Our explosive charges were cylinders 50 mm dia x 100 mm long. They were initiated by a detonator-booster system on one end of the cylinder axis. The detonation wave propagates from the booster at the detonation velocity, about 8 mm/ μ s, as a somewhat spherical wavefront to the other end of the charge. The density of the unexploded charge is about 1.7 g/cm³, the density in the detonation front is about 2.3 g/cm³, and the detonation pressure is about 245 000 atm. The detonation wave traverses the length of the charge in about 12 μ s. As the material detonates, the outer surface of the charge begins to expand into the external environment, in our case a large tank evacuated or filled with 1 atmosphere of Ar gas. The inner core of the detonated charge remains at a pressure near 100 000 atm for about 3 μ s after passage of the detonation wave, providing a considerable time for carbon coagulation within or very near the bulk diamond stability field (Figs. 1 and 2). The most common form of the equation of state (1,4) gives a temperature of 2600 K in the steady portion of the wave and a chemical composition of H₂O, CO₂, N₂, and solid C. Chemical products recovered from quenched detonations contain many other components (3,5). There is much discussion about processes that may occur during quenching and about how to recover true detonation products (3,5).

EXPERIMENTAL

The experimental details of the detonations have been described (4). In these detonation reactions, O and N are present as well as C and H. The atomic fractions can be seen from the formulas TNT: C₇H₅N₃O₆, RDX: C₃H₆N₆O₆, TATB: C₆H₆N₆O₆, NQ: CH₃N₄O₂, and AN: NH₄NO₃. Atomic ratios are much different than those of typical chemical vapor deposition (CVD) processes. The charge compositions were made by adding solid powders to molten TNT in the following weight percentages: #27: 40 TNT/60 RDX, #36: 50 TNT/50 AN, #60: 50 TNT/50 TATB, #63: 50 TNT/50 NQ, and #10/41: 50 TNT/50 NQ. The charges were fired in a cylindrical vessel 1.5 m³ in volume, either evacuated or filled with 1 atm of Ar gas (2,4). The soot was recovered from the vessel after the detonation of each charge. The soots were then oven dried at 105°C to constant weight.

The micromorphologies of the soots were recorded by transmission electron microscopy (TEM); the diamonds were recovered by oxidizing the soot with HNO₃/HClO₄ (4); the diamonds in the residue were identified by their x-ray diffraction (XRD) powder patterns, and the diameters of the recovered diamonds were determined with an x-ray diffractometer. Thermally labile components of the soot were measured with thermogravimetric analysis (TGA), and some of the components were identified with direct insertion probe mass spectrometry (DIP/MS) or gas chromatography with mass spectrometric (GC/MS) detection.

RESULTS AND DISCUSSION

TEM has shown that the soots are composed of graphite ribbons having a smallest dimension of 3-10 nm and sometimes of diamonds having diameters of 3-7 nm (4).

The interplanar spacings measured in these samples agree well with the spacings of bulk diamond.

The crude residue containing the diamonds was sometimes found by XRD to contain minor amounts of other materials such as Al_2O_3 , MgO , and SiO_2 knocked loose from the vessel walls. When diamonds were present, this residue amounted to 15-22 wt% of the dried soot. Diamonds were found by TEM and in the oxidation residues of samples #27, #60, and #63, but not in samples #36 and #10/41. The diameters of the diamonds in the oxidation residues were determined by the widths of their diffraction lines measured on an x-ray diffractometer, and in all three cases, they were equal to the diameter of the diamonds observed in the TEM images. The diameters determined in this manner were 7 nm in #27, 3 nm in #60 and 3 nm in #63.

No measurable residue was obtained from #10/41 (TNT/NQ), which was fired in a vacuum. This result can be compared with that of #63 (also TNT/NQ, but fired in 1 atm of Ar) where diamonds were found. Sample #10/41 underwent a process called reshock, whereby the detonation products expanding in the vacuum are shocked to a high temperature when they collide abruptly with the vessel wall. Typically this results in the reaction



advancing far to the right because it is favored by high temperature at low density (3). Perhaps the diamonds in sample #10/41 were consumed preferentially by reaction 1. When the vessel is filled with Ar gas, much of the kinetic energy of the expanding products is absorbed by the Ar, mitigating the effects of reshock.

The residue from #36 (TNT/AN) contained only a small amount of Al_2O_3 but no diamonds. We have no explanation for this at this time.

Neither the graphite nor the diamond morphologies observed in the detonation soots seem to fit the picture of growth by aggregation. The detonation graphite appears as ribbons a few nanometers thick, not as aggregated smaller particles or crystals (4). This observation can be contrasted with the reported structures of graphitic soots from hydrocarbon flames, which are typically spheres 10-500 nm in diameter, composed of many small graphitic crystallites a few nanometers thick (6). The detonation diamonds appear to be perfect single crystals 3-7 nm in diameter and not aggregates of smaller crystals. Furthermore, the sizes of the diamond and graphite particles observed in these detonations appear to be too small for unrestricted growth by aggregation.

A model for growth of carbon solid by diffusive aggregation in the detonation product environment has been developed by Shaw and Johnson (SJ) (7). We can apply the SJ model to these detonations with the aid of a hydrodynamic model for the expansion of the detonation products. The model for the expansion also has been described (8).

Figures 1 and 2 show computed hydrodynamic histories of some representative volume elements in the charges used here. A large portion of the charge is maintained at a density near the detonation density for a time of about 3×10^{-6} s, whereas the characteristic time for aggregation in the SJ model is 2×10^{-12} s. The ratio of these two times gives the number of atoms in the most probable particle size, which is 1.5×10^6 atoms. If the most probable particle were a crystalline diamond sphere it would be 26 nm in diameter, whereas the largest particle we see is only 7 nm. By the SJ model, the volume of the most probable particle size is proportional to aggregation time, so the difference between the model and observation is large. Conversely, the size observed could be attained in only 5×10^{-9} s, if unrestricted aggregation were the limiting mechanism. The differences suggest that particle growth has additional restrictions and that aggregation progresses in increments closer in size to atoms than to small crystals.

The small size of the diamonds and the graphite ribbons raise the possibility that surface chemistry may play a role in their relative stabilities. In a spherical diamond 3 nm in diameter 37% of the carbon atoms are on the surface. If this surface were particularly stable, diamond might be more stable than graphite even without a high-pressure environment. Unfortunately, we have no direct information about the diamond or graphite surfaces in the unaltered soot. Moreover, the information we do have suggests a broad range of possibilities for the chemistry of the diamond and graphite surfaces.

Gouy-balance measurements on the raw soot show evidence of unpaired electrons, a common feature of finely divided solid carbons. Elemental analysis of the dry soots shows the presence of H, N, and O in addition to C atoms. About 1/10 to 1/20 of the atoms are N and 1/10 to 1/50 are H. TGA analysis indicates that about 30% of the soot is heat-labile (Fig. 3). Initial results from DIP and GC/MS analyses of the gases driven off of soots with moderate heat (350-400°C) show mass spectra attributable to H_2O , NH_3 , CO_2 , CO , HCN , $HOCN$, urea, alkanes, alkenes, and polycyclic aromatics often substituted with $-CN$ and $-NH_2$ groups. DIP analysis indicates CO_2 and CO , in about a 2/1 molecular ratio, driven off a diamond residue recovered by the $HClO_4$ oxidation process. Auger/ESCA analysis of the recovered diamond residue shows the presence of N and O atoms that are removed by Ar-ion sputtering of the surface. This technique also shows that the interior of the recovered diamonds is made up of nearly pure C. These results show that the soot has a rich chemistry involving heteroatoms. The surfaces of the 3-nm diamonds contain only about 1% of the atoms in the original explosive. Given that a number of exotic chemical species have been found in the soot in quantities comparable to the number of surface atoms on the diamonds, it seems that surface chemistry of the diamonds is practically an open question.

Determining when in the hydrodynamic history (Figs. 1 and 2) the diamond growth takes place would also be of great interest.

CONCLUSIONS

Diamonds are now a well-established chemical product of the detonation process. The conditions under which they grow can be described. They appear as single crystals, not aggregates of smaller crystals, and their growth rate seems to be limited by something more than the diffusion of carbon precursors in the dense gaseous detonation products. Determination of the surface chemistry of the detonation diamonds and when in the hydrodynamic history their growth takes place remains to be done.

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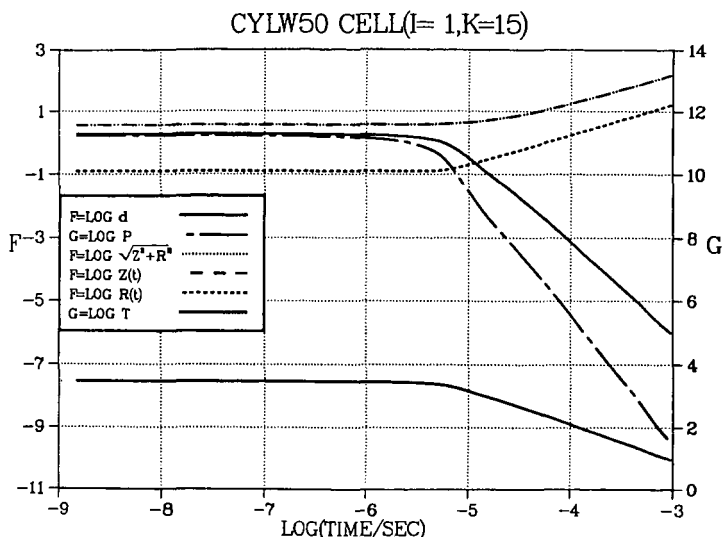


Figure 1. Hydrodynamic history of a volume element on the axis of the explosive charge 12.5 mm from the end opposite the booster charge. This volume element is representative of the detonation wave properties. The scales are logarithmic, and the units are CGS units, that is, density (d) is in g/cm^3 , pressure (P) is in dyne/cm^2 , coordinate of the volume element along the charge axis (Z) is in cm, coordinate along the charge radius (R) is in cm, and temperature derived from the equation of state (T) is in K. Log P is given on the G scale, where the value 11 represents 100 000 atm. Log P begins to depart from this value at about 3×10^{-6} s.

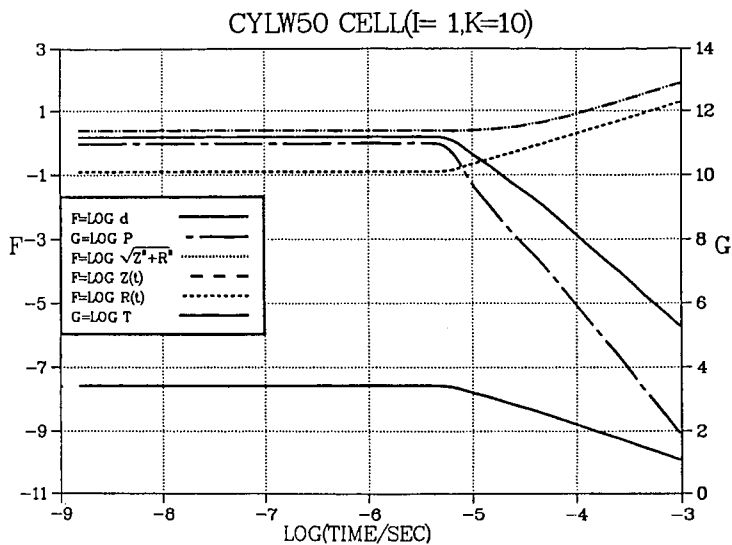


Figure 2. Hydrodynamic history of a volume element along the charge axis midway between the detonation wavefront and the booster (same scales and units as in Fig. 1). Log P is somewhat below 11 in this element, and it begins to drop below 11 after 5×10^{-6} s.

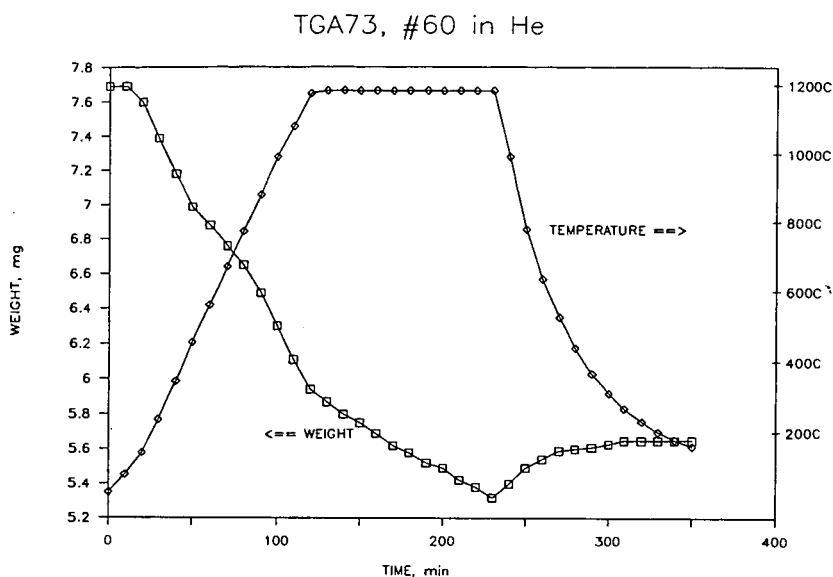


Figure 3. Thermogravimetric analysis of #60 in 1 atm of He gas. There is about 10% weight loss up to 400°C, the upper limit of the evolved gas analyses, and about 25% at the termination of the run at 1200°C.